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(72) Inventors ALFRED BUCK and KARL RATHGEB



## (54) PRODUCTION OF UREA

(71) We, INVENTA A.G. FUR FORSCHUNG UND PATENT-VERWERTUNG, a Swiss Body Corporate, of Stampfenbachstrasse 38, Zurich, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of producing urea in a reaction vessel in which the water content is kept low.

Prior art processes for the manufacture of urea from carbon dioxide and ammonia at elevated pressures and temperatures (for example, 170 bars and 180°C) are characterised in that, in addition to the urea formed, comparable amounts of unwanted products, principally carbamate, are also produced. In such processes, urea yields of up to 70 percent can be obtained if the pressure does not exceed 200 bars.

To separate the carbamate from the urea, the carbamate is decomposed with the aid of heat. Various methods are known for reintroducing into the reactor the resultant gaseous substances. One of the earliest of these known methods dates back to the 1950's and is based on the fact that under suitable conditions, ammonia can be selectively separated from carbon dioxide with the aid of an ammonium nitrate solution (cf. e.g., Swiss Patent No. 290,289; French Patent No. 1,085,316). Although this known process proved successful in industrial operations, it was soon replaced by less costly and more efficient processes (cf. e.g. U.S. Patent No. 3,317,601).

Common to all of these prior art methods is the separation of the carbamate at pressures lower than the reactor pressure in several stages, and the absorptive return into the pressure autoclave of the unconverted reactants.

Another method which has met with some success is the stripping process of Netherlands Staatsmijnen (see, e.g., U.S. Patent No. 3,356,723). This method utilizes the principle of counter-flow (countercurrent). The carbamate is decomposed and the resulting products are returned isobarically to the reactor.

All of these prior art processes are disadvantageous in that the melt in the reaction chamber contains a large amount of water and the conversion into urea relative to carbon dioxide at the outlet of the reactor is relatively low. Moreover, in all cases the urea must be released from the reaction water at low pressure and at low temperature. However, during prilling the melt must again be brought to a high temperature. All of these steps increase the energy requirement for the process and large unused quantities of energy are released directly into the environment at low temperatures. U.S. Patent No. 2,527,315 shows that through the use of a large excess of ammonia it is possible to obtain a urea-melt having a lower water content. However, the use of a large excess of ammonia requires extensive equipment and the input of considerable quantities of energy.

The present invention overcomes the disadvantages of the known processes. It should be noted that in developing this invention it was found that an NH<sub>3</sub> to CO<sub>2</sub> mole ratio of down to 2 could be employed. This is remarkable because it is now possible to dispense with the use of excess ammonia while maintaining very high urea yields. As the present invention is carried out continuously, the melt in the reactor is continually drained and the concentration of water kept low.

Surprisingly, it has been found that the free sub-critical water does not stay in the liquid phase, as would be expected, but instead is distributed almost equally between the two phases, liquid and gas. The ammonia, which is above its critical temperature, is surprisingly found to a large extent in the liquid phase; while carbon dioxide at higher temperatures prefers the gaseous phase almost exclusively.

Accordingly, the present invention provides a process for the continuous production of urea from the reaction of ammonia and carbon dioxide in a reactor. The process is characterized in that water is continuously removed from the urea melt in the reactor. Preferably, the water is removed at a rate such that the mol ratio of water to urea produced in the reactor is always less than 1, and this may be achieved by continually feeding the urea melt with a mixture of recirculated gases consisting of  $\text{CO}_2$ ,  $\text{NH}_3$  and  $\text{H}_2\text{O}$  which has been at least partially dried before entering the urea reactor.

Preferably the reaction temperature is at least  $160^\circ\text{C}$ , a temperature of  $170$ — $200^\circ\text{C}$  being most preferred. The preferred mole ratio of ammonia to carbon dioxide is 2:1.

The process of this invention has the following advantages:

1. The urea conversion in the melt relative to  $\text{CO}_2$  is large (e.g. 93% or more).
2. The content of water in the melt is very low.
3. There is a modest equilibrium of reaction pressure even at high temperatures.
4. Although the operation is effected without or with only a very slight excess of  $\text{NH}_3$ , the liquid phase is strongly alkaline, and therefore only small quantities of biuret are formed despite the low water content.
5. All the undesired compounds in the liquid phase can be decomposed into  $\text{NH}_3$  and  $\text{CO}_2$ . Thus it is possible, at a relatively low reactor pressure and low biuret content, to employ a high temperature. In this manner, a high reaction speed is achieved, a small reactor can be utilized and a small  $\text{CO}_2$  compressor output is required.

The process of the invention is preferably carried out by a method which will now be described with reference to the accompanying drawing, which is a schematic representation of the apparatus involved. The apparatus consists of a horizontally disposed reaction vessel 1, a vertical partial condenser 2, a gas circulating blower 3, a urea work-up unit 12, a separating unit 10 and piping (represented by connecting lines and arrows) belonging to the system.

The mode of operation of this process is as follows: The water-saturated gas leaves reaction vessel 1 and reaches partial condenser 2 at its lower end via a short pipe 4, which is hydrodynamically well designed. Together with the constituents flowing in from pipe 5 (described below) the mixture of gases is conveyed upwardly through the condenser tubes, being partially condensed as the temperature falls in the direction of flow. The ascending saturated vapour is consequently conveyed in counter-current relationship to the film of condensate trickling down the walls, the condensate accumulating at the lower end of the condenser 2 surprisingly showing a very high concentration of water. This condensate also contains carbamate. The water is separated in separating unit 10 and drawn off via the pipe 11. The gaseous carbamate mixture is conveyed into the condenser 2 via the pipe 6. The uncondensed vapour, now low in water, is drawn in by the circulating blower 3 (together with the mixture entering from the pipe 6 if this has been introduced into the upper part of the condenser 2 as shown in the drawing), and introduced tangentially into the urea melt at a plurality of points at the periphery of the reaction vessel 1 via the pipe 7. By momentum exchange between the gas and the liquid, the latter is kept in rotary movement, in such manner, in fact, that in the interior of the reaction vessel 1 there is formed a ring of liquid from the hollow space of which the saturated vapour mixture is drawn off towards the partial condenser 2. The gas circuit described is thereby closed. From the reaction vessel 1, the urea is conveyed together with  $\text{CO}_2$ ,  $\text{NH}_3$  and  $\text{H}_2\text{O}$  via the pipe 9 into the work-up unit 12 and is separated therein in known manner, the urea being drawn off through the pipe 13 and the other constituents flowing into the gas circuit through pipe 5 into pipe 4.

The reaction vessel 1 is preferably placed in a horizontal position. As is apparent from the foregoing, it is desirable to bring the gas entering the reaction vessel and low in water into intensive contact with the urea melt in order to saturate the gas with as much water as possible. This operation could be suitably carried out in a vertical bubble column. In order to keep investment costs low, pressure apparatus of small diameter is preferred. For a given residence time, however, the bubble-column reaction vessel and, consequently, the static liquid pressure acting on the bottom of the reaction vessel, becomes high. This static and very important liquid pressure must be supplied, in addition to the other pressure losses occurring in the circulating system, by the circulating blower 3, whereby its energy requirements increase markedly. Due to the horizontal reaction vessel with the melt revolving at above-critical speed, a liquid ring is obtained. If this ring is developed, then there

is obtained, together with the length of reaction vessel in accordance with the above residence time, a layer of liquid with a considerable base area and of small height or depth. The area increases with increasing length of the reaction vessel. In accordance with the small layer height (ring thickness), the feed or charging of this layer with gas requires a comparatively small energy consumption. The large reaction vessel surface (base area) may have a large number of tangentially drilled holes through which the melt is intensively charged with gas in consequence of the large area of the bubbles formed. This arrangement consequently avoids high energy requirements by the circulating blower 3 with low investment costs for the reaction vessel 1. At the same time, an equal residence time and an equally intensive exchange of substances is ensured in comparison with a bubble column. The advantage achieved in this way is decisive for the economy of the method, since the circulating mass of gas for an average 500 tons per day plant, is, for example, 650 tons per hour. Another advantage of the method is that the heat liberated by the partial liquefaction of the gas can be used for generating 6-bar steam.

Examples 1—4 are batchwise experiments in which an  $\text{NH}_3/\text{CO}_2$  molar ratio of 2:1 was employed. The ratio of water and urea introduced to the autoclave to the volume of the reactor was 530 kg/m<sup>3</sup>. The mole ratio of  $\text{H}_2\text{O}:\text{CO}_2$  was varied between 0.5:1 and 1:1.

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**Example 1**

$\text{H}_2\text{O}/\text{CO}_2$  mole ratio=1 Temperature=160°C  
The  $\text{H}_2\text{O}/\text{CO}_2$  mole ratio refers to the liquid *and* the gaseous phase. The experiments were carried through isochorically.

With these parameters the following results are obtained:

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Pressure=85 bars

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Composition of liquids (w'=percentage by weight):

$$w'_{\text{urea}}=37.8 \quad w'_{\text{NH}_3}=25.4 \quad w'_{\text{CO}_2}=24.8 \quad w'_{\text{H}_2\text{O}}=11.3 \quad w'_{\text{water}}=0.7$$

Composition of gases (w''=percentage by weight):

$$w''_{\text{NH}_3}=18.8 \quad w''_{\text{CO}_2}=78.7 \quad w''_{\text{H}_2\text{O}}=2.5$$

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Urea conversion in the melt relative to  $\text{CO}_2$ =60.4%

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**Example 2**

$\text{H}_2\text{O}/\text{CO}_2$  mole ratio=1 Temperature=170°C

Pressure=120 bars

Composition of liquids (w'=percentage by weight):

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$$w'_{\text{urea}}=40.7 \quad w'_{\text{NH}_3}=23.3 \quad w'_{\text{CO}_2}=23.1 \quad w'_{\text{H}_2\text{O}}=11.5 \quad w'_{\text{water}}=1.4$$

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Composition of gases (w''=percentage by weight):

$$w''_{\text{NH}_3}=18.1 \quad w''_{\text{CO}_2}=77.1 \quad w''_{\text{H}_2\text{O}}=4.80$$

Urea conversion in the melt relative to  $\text{CO}_2$ =63.8%

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**Example 3**

$\text{H}_2\text{O}/\text{CO}_2$  mole ratio=0.63 Temperature=170°C

With these parameters the following results are obtained:

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Pressure=108 bars

Composition of liquids (w'=percentage by weight):

$$w'_{\text{urea}}=55.3 \quad w'_{\text{NH}_3}=23.7 \quad w'_{\text{CO}_2}=16.8 \quad w'_{\text{H}_2\text{O}}=2.5 \quad w'_{\text{water}}=1.7$$

Composition of gases (w''=percentage by weight):

$$w''_{\text{NH}_3} = 23.1 \quad w''_{\text{CO}_2} = 72.0 \quad w''_{\text{H}_2} = 4.9$$

Urea conversion in the melt relative to  $\text{CO}_2 = 76.7\%$

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**Example 4**

$\text{H}_2\text{O}/\text{CO}_2$  mole ratio=0.63 Temperature=180°C  
With these parameters the following results are obtained:

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Pressure=127.5 bars

Composition of liquids (w'=percentage by weight):

$$w'_{\text{urea}} = 64.6 \quad w'_{\text{NH}_3} = 24.8 \quad w'_{\text{CO}_2} = 5.0 \quad w'_{\text{H}_2} = 3.3 \quad w'_{\text{water}} = 2.3$$

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Composition of gases (w''=percentage by weight):

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$$w''_{\text{NH}_3} = 21.2 \quad w''_{\text{CO}_2} = 76.2 \quad w''_{\text{H}_2} = 2.6$$

Urea conversion in the melt relative to  $\text{CO}_2 = 92.8\%$

**Example 5**

This Example illustrates the continuous operation of the present invention. Reference to the apparatus corresponds to the accompanying drawing.

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For an output of 500 tons of urea per day, reaction vessel 1 is fed with 4.24 kg/s  $\text{CO}_2$  and 3.28 kg/s  $\text{NH}_3$ .

The pressure in the reaction vessel is 125 bars and the temperature is adjusted to 180°C. The gas circulates in the circuit 1→4→2→3→7. The gas leaving the reaction vessel through pipe 4 consists of 136.4 kg/s  $\text{CO}_2$ , 37.95 kg/s  $\text{NH}_3$  and 4.65 kg/s  $\text{H}_2\text{O}$ .

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When this gas stream is combined with the constituents coming from the urea work-up unit by way of pipe 5, 136.83 kg/s  $\text{CO}_2$ , 40.09 kg/s  $\text{NH}_3$  and 4.93 kg/s  $\text{H}_2\text{O}$  enter the lower part of the partial condenser 2 at a temperature of 180°C. This apparatus is operated at the same pressure as the reaction vessel, the heat being carried off in the jacket by 6-bar steam. The liquid leaving the tubes (through pipe 8) consists of 2.7 kg/s  $\text{CO}_2$ , 2.08 kg/s  $\text{NH}_3$  and 1.86 kg/s  $\text{H}_2\text{O}$ .

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The mixture of gases drawn in by the blower (composed of gas from pipe 6 and gas not condensed in condenser 2) has a temperature of 165°C and contains 136.83 kg/s  $\text{CO}_2$ , 40.09 kg/s  $\text{NH}_3$  and 3.2 kg/s  $\text{H}_2\text{O}$ , this being returned to reaction vessel 1 through pipe 7. The melt leaving the reaction vessel through pipe 9 consists of the following mixtures:

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5.78 kg/s urea, 0.43 kg/s  $\text{CO}_2$ , 2.14 kg/s  $\text{NH}_3$  and 0.28 kg/s  $\text{H}_2\text{O}$ .

This mixture is split up by a work-up unit 12, known in the art, the urea being drawn off through pipe 13, while the other constituents are introduced into the gas circuit (through pipe 5) into pipe 4.

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**WHAT WE CLAIM IS:—**

1. A process for continuously preparing urea from ammonia and carbon dioxide in a reaction vessel characterised in that water is continuously removed from the urea melt in the reaction vessel.

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2. A process according to claim 1 in which the molar ratio of water to the urea produced in the reaction vessel is always less than 1.

3. A process according to claim 1 or claim 2 in which the reaction temperature in the reaction vessel is at least 160°C.

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4. A process according to claim 3 in which the reaction temperature is 170 to 200°C.

5. A process according to any preceding claim in which the molar ratio of ammonia to carbon dioxide is 2:1.

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6. A process according to any preceding claim in which the removal of the water is made from the reaction mixture while the reaction progresses.

7. A process according to any preceding claim in which part at least of the gases present in the reaction vessel are withdrawn from the reaction vessel, some at least

of the water in the withdrawn gases is removed therefrom, and the thus dried gases are recycled to the reaction vessel.

8. A process according to claim 7 in which the removal of water is effected in a partial condenser.

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9. A process according to claim 8 in which the withdrawn gases pass through the condenser in counter-current relationship to the water removed from the gases.

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10. A process according to claim 8 or claim 9 in which the gases in the condenser are at substantially the same pressure as the pressure in the reaction vessel.

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11. A process according to any of claims 7 to 10 in which the reaction vessel is horizontally disposed.

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12. A process according to claim 11 in which the dried gases are introduced tangentially into the reaction vessel and the urea melt is thereby set in rotary motion.

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13. A process according to claim 1 substantially as herein described with reference to the accompanying drawing.

14. Urea when made by a process according to any preceding claim.

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For the Applicants:  
GILL JENNINGS & EVERY,  
Chartered Patent Agents,  
53-64 Chancery Lane,  
London WC2A 1HN.

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